

# A Further Investigation of the Chlorides of Orthosulpho- benzoic Acid.

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## DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE  
JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH  
THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY.

BY

PHILIP HOWARD COBB.

BALTIMORE, MD.

1905.

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THE ESCHENBACH PRINTING CO.  
EASTON, PA.





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## A FURTHER INVESTIGATION OF THE CHLORIDES OF ORTHOSULPHOBENZOIC ACID.

### I. INTRODUCTION.

In 1889 Remsen and Dohme<sup>1</sup> allowed phosphorus pentachloride to react with the acid ammonium salt of orthosulphobenzoic acid. The chloride thus obtained was submitted to investigation. Its reactions with water, alcohols and ammonia were studied, and no evidence was obtained to cast doubt upon its chemical individuality. Remsen and Coates<sup>2</sup> studied the reaction of anilin upon the chloride, and obtained two isomeric products of the composition  $C_{19}H_{16}N_2SO_3$ . This led them to advance the hypothesis that the chloride thus prepared was in reality a mixture of two isomeric chlorides, one of the symmetrical, the other of the unsymmetrical structure. Remsen and Kohler<sup>3</sup> continued the work, and succeeded in isolating one of the constituents of the mixture in fairly pure condition. They found it to be a well crystallized substance melting at  $76^\circ$ . The other was obtained as an oil which did not crystallize. Later Remsen and Saunders<sup>3</sup> obtained the same chloride in crystalline form. It melted at  $21^\circ.5-22^\circ.5$ . Remsen and McKee<sup>4</sup> continued the work and were able to isolate the high-melting chloride in pure condition (melting-point  $79^\circ-79^\circ.5$ ). By crystallization of the mixed chlorides from ligroin they also obtained the chloride melting at  $21^\circ.5-22^\circ.5$ . The melting-point could not be changed by repeated crystallization. Though this substance was afterward shown to be composed of equal molecules of the high-melting chloride and another melting at  $40^\circ$ , the constituents seem to be held in loose chemical combination rather than in mechanical mixture. In the next year Remsen and Chambers<sup>5</sup> discovered that the chlorides could be separated by ammonia and the high-melting one obtained pure. In 1898 List and Stein<sup>6</sup> showed that the chloride melting at

<sup>1</sup> Am. Chem. J. **11**, 332.

<sup>2</sup> *Ibid.*, **17**, 309.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Am. Chem. J. **18**, 794.

<sup>5</sup> *Ibid.*, **18**, 791.

<sup>6</sup> Ber. d. Chem. Ges. **31**, 1648.

21°.5-22°.5 was not pure, but that it consisted of a mixture of a chloride melting at 79°.5 and another melting at 40°. They effected the separation by distilling the mixture under reduced pressure, and also originated the method which is now employed for the preparation of the low-melting chloride.

The action of the various reagents on the chlorides has been carefully studied<sup>1</sup> and the conclusion reached that to the high-melting chloride the symmetrical formula must be assigned, while the low-melting chloride has received the unsymmetrical formula. While the evidence for the symmetrical nature of the former has been made clear, in the case of the latter more difficulty has been found in arriving at any definite conclusion. The products derived from the high-melting chloride are usually well characterized and their structures point definitely to the symmetrical nature of the chloride. Those derived from the low-melting chloride on the other hand, while sometimes characteristic, are often identical with those derived from its isomer, a fact which has made the problem a difficult one with which to deal.

## *II. Preparation of Materials.*

The derivatives of orthosulphobenzoic acid employed in this investigation were prepared by methods which have been fully described by previous workers. No changes were introduced except in the preparation of the low-melting chloride, which will be described. Other reagents employed, sodium ethylate, phosphorus oxychloride and thionyl chloride, and the organic anhydrides were prepared by the usual methods.

### *Preparation of the Low-Melting Chloride.*

The method formerly employed for the preparation of the low-melting chloride consisted in heating the neutral potassium salt with phosphorus oxychloride in a sealed tube for five hours or more. The temperature was not allowed to exceed 135°, since orthochlorbenzoyl chloride is formed at this point. The method here employed differs from the above only in that the mixture is heated in a flask and not under pressure. It was worked out by Mr. K. G. Falk.

<sup>1</sup> Remsen : Am. Chem. J. 30, 247.



One hundred grams of the dried and finely pulverized neutral potassium salt are placed in a 250 cc. round-bottomed flask and 80 grams (1.5 mols.) phosphorus oxychloride are added. After thoroughly mixing the materials, a cork bearing an air condenser is inserted in the neck of the flask, and the whole is heated in a bath of sulphuric acid or paraffin for fourteen hours at  $130^{\circ}$ . At the end of this time the mass is removed from the flask by a spatula and on cooling is ground with ice water in a mortar.

This treatment is necessary in order to remove the excess of the oxychloride and also the potassium chloride formed in the reaction. The washing is repeated several times. The undissolved portion which settles to the bottom of the mortar consists largely of the low-melting chloride. It is filtered off in a Buchner funnel provided with a muslin filter. After drying as thoroughly as possible on a porous plate the chloride is crystallized from ligroin. The melting-point of the pure substance is  $40^{\circ}$ . A second crystallization may be necessary.

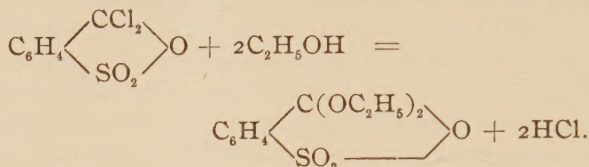
As it is impossible to dry the chloride thoroughly by means of a porous plate, and since the water remaining interferes considerably with the crystallization, it has been found advantageous to dissolve the chloride in ether at this point, and after filtering off any insoluble matter to dry the ethereal solution over calcium chloride as in the case of the high-melting chloride. After filtration the ether is distilled off and the chloride crystallized as before.

### *III. The Action of Hydrochloric Acid on Organic Anhydrides.*

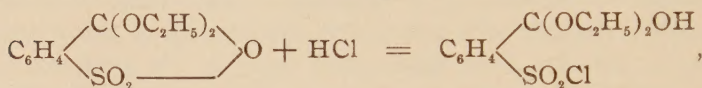
The action of alcohols on the low-melting chloride, in the cold, has been shown to consist in the formation of symmetrical ester chlorides, a fact which, taken by itself, would be a strong argument for the symmetrical structure of the chloride. In the light of the other evidence, however, it is plain that this reaction is not decisive, and in view of the fact that all of the distinguishing reactions show that the low-melting chloride is unsymmetrical, there must be some other explanation for the peculiar action of alcohol. It is always possible to assume a molecular rearrangement, but a more satisfactory hypothesis was suggested by Remsen.<sup>1</sup> The suggestion is this: When

<sup>1</sup> Am. Chem. J. 30, 247.

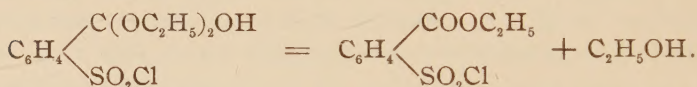
ethyl alcohol is allowed to act upon the low-melting chloride, the first step in the reaction would naturally be the substitution of two ethoxy groups for the chlorine atoms, thus :



The anhydride might then take up hydrochloric acid,



and the product thus formed would lose alcohol and pass into the ester chloride :



In order to test this view experimentally, the action of dry hydrochloric acid on various organic anhydrides was tried. Experiments of this kind have already been made with acetic,<sup>1</sup> benzoic,<sup>2</sup> benzoic-acetic<sup>3</sup> and some other acids, but no experiments with the anhydrides of dibasic acids or inner anhydrides have been recorded. It appears that the anhydrides of monobasic acids react readily with dry hydrochloric acid. Attention was now turned to the inner anhydrides.

From the experiments performed it is evident that the anhydrides of the dibasic acids studied do not react with dry hydrochloric acid, while those of monobasic acids are easily attacked. Therefore the formation of symmetrical ester chlorides, by the action of alcohol on the low-melting chloride, does not seem to be dependent upon the presence of hydrochloric acid. The formation of symmetrical esters by the action of sodium ethylate upon the low-melting chloride also seems to furnish an argument against this explanation.

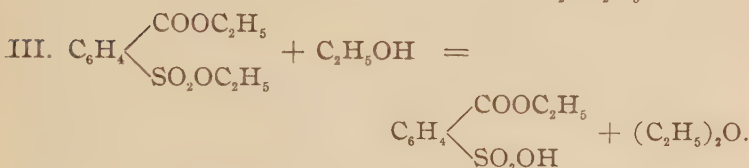
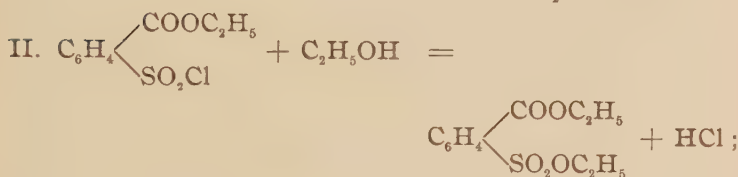
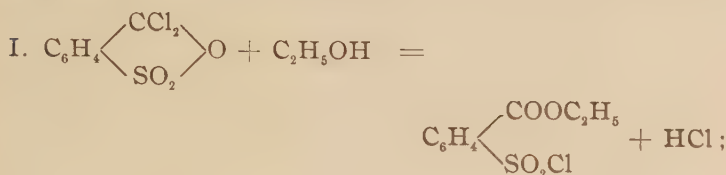
<sup>1</sup> H. Gal : Ann. Chim. Phys., [3], **66**, 187.

<sup>2</sup> Mosling : Ann. Chem. (Liebig), **118**, 303.

<sup>3</sup> Green : Bull. Soc. Chim., **33**, 426.

IV. *The Action of Alcohols and Alcoholates on the Chlorides.*

The action of alcohols upon the chlorides has been previously studied in this laboratory,<sup>1</sup> as well as elsewhere,<sup>2</sup> and it has been shown that the first products formed are ester chlorides which, upon further action of the alcohol, are transformed into the ester acids:



With the low-melting chloride the ester chloride is easily formed, while its isomer is only slowly attacked by cold alcohol.

The work along this line was continued by R. M. Bird,<sup>3</sup> who studied the action of the alcoholates as well. A brief summary of his results is as follows: The low-melting chloride, when dissolved in cold methyl alcohol, passed into the orthosulphone chloride and methyl benzoate. Upon evaporating the solution the substance separated in small, diamond-shaped crystals which melted at 57°–58° (corr.). They were soluble in alcohol and ether, but insoluble in water. Cold dilute sodium hydroxide did not affect the substance, but upon boiling it dissolved and chlorine was removed.

<sup>1</sup> Remsen and Dohme: *Am. Chem. J.* **11**, 341. Remsen and Karslake: *Ibid.*, **18**, 825.

<sup>2</sup> List and Stein: *Ber. d. chem. Ges.*, **31**, 1659.

<sup>3</sup> *Am. Chem. J.* **30**, 247.

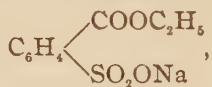


When the low-melting chloride was dissolved in methyl alcohol and the alcohol immediately boiled off, the orthosulphonic acid of methyl benzoate was obtained. Another product of this reaction was an oil which was shown to contain chlorine, and to it was assigned the formula of the orthosulphone chloride of methyl benzoate above described. It is, however, not stated that the oil became crystalline.

The orthosulphone chloride of ethyl benzoate was obtained by treating the dry, low-melting chloride with an alcoholic solution of sodium ethylate, until no more sodium chloride was precipitated. Upon extraction with ether and evaporation of the solvents, an oil remained which was insoluble in water, but soluble in alcohol and ether. When boiled with water it was hydrolyzed to an acid and hydrochloric acid was liberated. Treatment with ammonia yielded the orthosulphone amide of ethyl benzoate.

What was, apparently, the same oil was obtained by treating an alcoholic solution of sodium ethylate with an ethereal solution of the low-melting chloride. As a by-product of this reaction another oil was obtained which answered the description of the diethyl ester of orthosulphobenzoic acid obtained by Remsen and Dohme.<sup>1</sup> It was soluble in water, alcohol and ether, and contained no chlorine.

By this same treatment and 2 hours' standing before examining the products, the sodium salt of the formula,



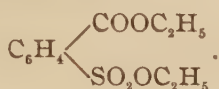
was formed.

A slightly warm solution of 1.070 grams of sodium ethylate, in absolute alcohol, was gradually added to 1.996 grams of the low-melting chloride, in ethereal solution. The reaction progressed until one-half of the ethylate had been added, when it suddenly stopped and could be induced to go no further. The resulting product was an oil. With dry ammonia, crystals were produced which melted at 225°–226°. They were acid toward litmus and potassium carbonate. The crystals gave a product with a sweet taste when boiled with concentrated am-

<sup>1</sup> Am. Chem. J. 11, 332.

monia, as also did the oil when treated in the same manner. Upon boiling the oil with water it was hydrolyzed to an acid. No formula was assigned to the substance.

An excess of ethyl alcohol was added to the low-melting chloride and boiled for 35 minutes. There resulted nothing but a neutral oil, which was soluble in water, alcohol and ether; it contained no chlorine. Upon boiling with sodium hydroxide, ethyl alcohol was formed. The formula assigned was that of the diethyl ester,



None of the compounds above described, with the exception of the orthosulphone chloride of methyl benzoate and the sodium salt of ethyl orthosulphobenzoate, were analyzed. Certain considerations made it seem well to repeat the work :

1. The formation of ester chlorides by the action of sodium ethylate on the chlorides, and the impossibility of causing the reaction to go further.

2. The solubility of the so-called diethyl esters in water.

3. The production of a substance of acid reaction by boiling with ammonia.

4. The impossibility of obtaining the ester of a sulphonic acid by boiling its chloride with alcohol. Sulphonic acid esters are saponified by this process.

*Action of Methyl Alcohol on the Low-Melting Chloride.*—Ten grams of the low-melting chloride were dissolved in 30 or 40 cc. of cold methyl alcohol, and the solution allowed to stand 2 hours. At the end of that time the alcohol was evaporated by warming the solution and drawing air through it. When the proper concentration had been reached, very small, diamond-shaped crystals separated from the solution. The evaporation was continued until no more crystals deposited, when they were filtered off and washed with water to remove the alcohol and hydrochloric acid which is formed in the reaction. The substance agreed in most of its properties with that prepared by Bird. It is soluble in alcohol and ether, but insoluble in water. Cold alkali, whether concentrated or dilute, has

no effect upon the compound, but on boiling it dissolves and chlorine is removed. The melting-point,  $63^{\circ}$ – $64^{\circ}$  (uncorr.), is rather higher than that given by Bird, but it is probable that his material was somewhat impure, since his figures differ considerably from the calculated values.

Analysis<sup>1</sup>:

0.1062 gram substance gave 0.1592 gram  $\text{CO}_2$  and 0.0276 gram  $\text{H}_2\text{O}$ .

0.2354 gram substance gave 0.2401 gram  $\text{BaSO}_4$  (Carius).

To determine the chlorine the substance was saponified by heating with pure sodium hydroxide and titrated to neutrality with nitric acid. The chlorine was then determined with a 0.1 N solution of silver nitrate. Sodium chromate was used as the indicator:

0.1835 gram substance required 7.8 cc. 0.1 N  $\text{AgNO}_3$ .

|    | Calculated for<br>$\text{C}_6\text{H}_4\begin{matrix} \text{COOCH}_3 \\ \text{SO}_2\text{Cl} \end{matrix}$ | Found. |
|----|------------------------------------------------------------------------------------------------------------|--------|
| C  | 40.90                                                                                                      | 40.88  |
| H  | 3.01                                                                                                       | 2.92   |
| Cl | 15.11                                                                                                      | 15.06  |
| S  | 13.66                                                                                                      | 14.00  |

The reaction is to be expressed as follows:



The action of boiling ethyl and methyl alcohols has been fully investigated by former workers.<sup>2</sup> The reaction with methyl alcohol was repeated and the product was found to be the ester acid. No trace of the oil containing chlorine, as described by Bird, was obtained. The analogous reactions with ethyl alcohol have already been given.

*Action of Methyl Alcohol on the High-Melting Chloride.*—On the high-melting chloride the alcohols, in general, react with less ease than upon the low-melting chloride. Upon boiling, however, the ester acids are also produced.

<sup>1</sup> The method employed for the determination of carbon and hydrogen was that described by Morse and Taylor: *Am. Chem. J.* **33**, 591. See also L. S. Taylor, Dissertation, J. H. U., 1905.

<sup>2</sup> Remsen and Dohme: *Ibid.*, **11**, 341. Remsen and Karslake: *Ibid.*, **18**, 825.



*Action of Boiling Ethyl Alcohol on the Chlorides.*—By boiling either chloride with 95 per cent ethyl alcohol for some hours, Bird obtained an acid of which the barium salt contained from 28 to 29.5 per cent of barium. Humphreys<sup>1</sup> had already obtained the same acid by boiling the orthosulphone chloride of phenyl benzoate for 12 hours, in absolute alcohol.

In the course of the present investigation the reaction described by Bird was repeated, with the hope of obtaining some light on the composition of this acid. Five grams of the high-melting chloride were boiled for 13 hours with absolute ethyl alcohol. The formation of ethyl chloride was continuous. After the reaction was over the alcohol was distilled off, and the remaining hydrochloric acid was expelled by heating on the water-bath. The product was dissolved in water, filtered from the small insoluble residue and boiled with barium carbonate until no more was dissolved. After crystallization the salt was dried and analyzed for barium; 0.1800 gram of substance gave 0.868 gram  $\text{BaSO}_4$ . Found: Ba, 28.37 per cent. This was evidently the same acid that had been obtained by Humphreys and Bird. Since no formula could be assigned to the substance from the analysis of its barium salt, an effort was made to learn its structure in another way. The experiment was repeated with an equal quantity of the chloride and the barium salt prepared as before. This was converted into the sodium salt and, after evaporating to dryness, the salt was treated with phosphorus pentachloride. Reaction took place immediately. After heating some time to expel the oxychloride, water and ice were added and the material was ground until all traces of the oxychloride had been removed. After washing several times with water, strong ammonia was added and the mixture was warmed on the water-bath. The solutions became sweet and, with hydrochloric acid, gave a heavy precipitate of saccharin. This experiment pointed to the presence of orthosulphobenzoic acid. The following considerations lead to the same conclusion: The action of boiling alcohol on the chlorides is known to produce the ester acid. Further action of the alcohol yielded the unidentified acid. The action of alcohol on the phenyl ester

<sup>1</sup> Dissertation, J. H. U., 1900.

chloride must first convert it into the ester acid. Upon further boiling, the unidentified acid was also formed. These facts show that a change in the carboxyl group must have taken place. The action of phosphorus pentachloride, already referred to, showed the acid to be dibasic. The ethyl esters of carboxyl acids are not saponified by absolute alcohol, however, and a special reason must be sought in this case. It has been stated that ethyl chloride was formed constantly and for every molecule of ethyl chloride 1 molecule of water must have resulted. The tendency of the water should be to saponify the ester and there would result an equilibrium between orthosulphobenzoic acid and the ester acid. In the experiments performed by Bird he obtained the acid after boiling with 95 per cent alcohol for 3 hours, while in the experiments last described it was necessary to heat with absolute alcohol for 13 hours. Providing that all of the hydrochloric acid formed in this reaction reacted with the alcohol, then, for every molecule of chloride used, enough water would be formed to saponify 2 molecules of the ester acid. The presence of the alcohol would cause an equilibrium to exist between the ester acid and orthosulphobenzoic acid. It appears, therefore, that the salt containing about 28 per cent barium is probably a mixture of a salt of orthosulphobenzoic acid and a salt of the ester acid.

#### *V. Action of Sodium Ethylate on the Chlorides.*

*High-Melting Chloride.*—Five grams of the high-melting chloride were dissolved in dry ether and an alcoholic solution of sodium ethylate was gradually added until the reaction ceased. The experiment is best carried out in a bottle, which may be corked and well shaken from time to time, because the precipitated sodium chloride is voluminous and interferes with the reaction. In no case were less than 2 molecules of ethylate required. The action never stopped half way, and the addition of an excess of ethylate was often found necessary in order that the reaction might be complete. After the action was over, the resulting mixture was poured into a separating-funnel containing acidulated water. The contents were thoroughly shaken until the sodium chloride and excess of ethylate were dissolved, when the aqueous layer was run off. The

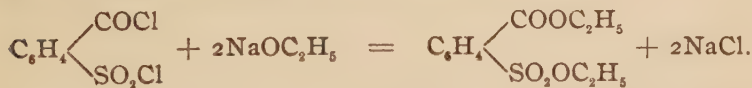
etheral layer was washed several times with water, then removed and dried over calcium chloride for 12 hours. After filtration and evaporation of the ether an oil remained which was soluble in alcohol and ether, but insoluble in water. It was neutral to litmus. Various methods for its purification were tried, but none was successful until distillation under reduced pressure was employed. Analysis:

0.1540 gram substance gave 0.2899 gram  $\text{CO}_2$  and 0.0738 gram  $\text{H}_2\text{O}$ .

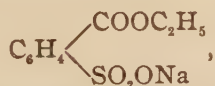
0.3493 gram substance gave 0.3243 gram  $\text{BaSO}_4$ .

|   | Calculated for<br>$\text{C}_6\text{H}_4\begin{cases} \text{COOC}_2\text{H}_5 \\ \text{SO}_2\text{OC}_2\text{H}_5 \end{cases}$ | Found. |
|---|-------------------------------------------------------------------------------------------------------------------------------|--------|
| C | 51.12                                                                                                                         | 51.33  |
| H | 5.47                                                                                                                          | 5.37   |
| S | 12.41                                                                                                                         | 12.74  |

These values point conclusively to the formula of the diethyl ester. It boils at  $212^\circ\text{--}213^\circ$  (21 mm.). At this pressure the ester distils with very little decomposition. It should be allowed to stand after distillation, for some hours, as a few crystals of sulphobenzoic anhydride usually separate. They can be removed by filtration. At a greater pressure, however, the ester distils with much decomposition. Among the products formed are sulphobenzoic anhydride and ethyl benzoate. The former was identified by its melting point ( $129^\circ.5$ ), and by its conversion into sulphonefluorescein when fused with resorcinol. The ethyl benzoate was detected by its odor. The reaction is expressed by the equation:



The yield of ester by this method was always small. The fact, established by Bird, that when the mass is allowed to stand a salt of the formula,



is formed, suggested the explanation of the small yield. The alcohol used as the solvent for the ethylate would tend to



saponify the ester, and the acid thus formed would be converted into its sodium salt by the action of the ethylate. To test this point the experiment was repeated as above, except that no alcohol was used, the ethylate being added in the dry state to the ethereal solution of the chloride. The yield of ester was almost theoretical. No sulphone chloride was obtained in the experiments.

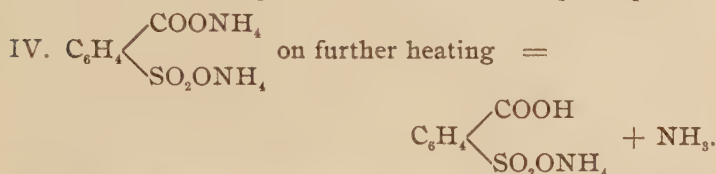
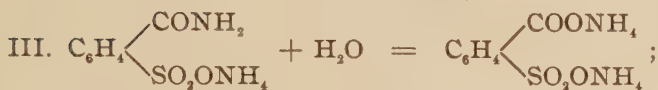
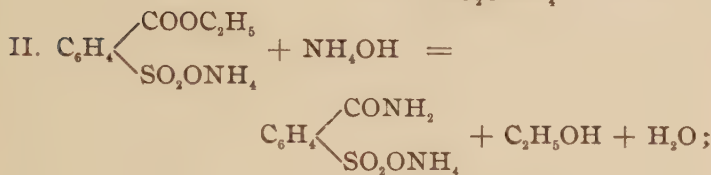
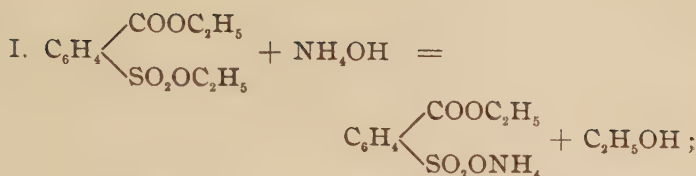
Upon boiling the impure ester with ammonia a sweet compound was usually produced, and sometimes a precipitate of saccharin appeared upon acidification. No such reaction takes place with the pure ester, however. Furthermore, the impure ester always gives a test for chlorine, while the pure substance is entirely free from it. These facts show that a small quantity of unchanged chloride is usually present in the impure ester. They also tend to explain certain observations made by Bird, which have already been referred to.

It is a fact that the action of ammonia upon the ester produces a substance which has an acid reaction. The ester is boiled, with frequent additions of concentrated ammonia, until it dissolves. This operation requires half an hour or longer. The solution is then evaporated to the proper concentration and allowed to cool. If the ammonia gas has all been expelled from the solution, the acid ammonium salt of orthosulphobenzoic acid separates. A determination of the nitrogen in the salt showed this to be the case.

0.1097 gram substance gave 0.006858 gram N (absolute).

|   |                                                                                                                       |                |
|---|-----------------------------------------------------------------------------------------------------------------------|----------------|
|   | Calculated for                                                                                                        |                |
|   | $\begin{array}{c} \text{COOH} \\ \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \\ \text{SO}_2\text{ONH}_4 \end{array}$ |                |
| N | 6.40                                                                                                                  | Found.<br>6.25 |

In order to obtain confirmatory evidence, if possible, a quantity of the acid ammonium salt of orthosulphobenzoic acid, which had been made by the hydrolysis of saccharin, was dissolved in an excess of strong ammonia and the solution evaporated. After the odor of ammonia had disappeared the solution was found to have become acid and crystals of the acid ammonium salt were obtained upon further evaporation. Ammonium sulphobenzoate was found to behave in the same way. The reactions must be expressed as follows :



With saponifying agents, the first point of attack is the sulphonic acid group. With aqueous alkali the ester is only slowly changed owing to its insolubility in water, but when alcoholic alkali is employed the reaction proceeds with ease. The final product of the action of alkalis is the neutral salt of orthosulphobenzoic acid. Aqueous ammonia acts more easily than aqueous alkali.

*Low-Melting Chloride.*—The action of sodium ethylate on the low-melting chloride also results in the formation of the diethyl ester. The ester agrees in all its properties with the one prepared from the high-melting chloride. Analysis:

0.1537 gram substance gave 0.2863 gram  $\text{CO}_2$  and 0.0794 gram  $\text{H}_2\text{O}$ .

|   | Calculated for<br>$\text{C}_6\text{H}_4 \begin{array}{l} \text{COOC}_2\text{H}_5 \\ \text{SO}_2\text{OC}_2\text{H}_5 \end{array}$ | Found. |
|---|-----------------------------------------------------------------------------------------------------------------------------------|--------|
| C | 51.12                                                                                                                             | 51.46  |
| H | 5.47                                                                                                                              | 5.86   |

The reaction was tried under various conditions, an alcoholic solution of sodium ethylate was added to the dry chloride;

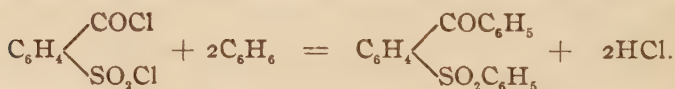
the chloride, in ether, was treated with an alcoholic solution of the ethylate, and, finally, dry ethylate was added to an ethereal solution of the chloride. The last was found to be the most satisfactory method.

The neutral oils soluble in water, which are described by Bird, have not been obtained.

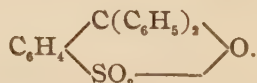
On grinding together dry sodium ethylate and dry, low-melting chloride, Bird obtained a product that he was not able to identify. The reaction is explosive and difficult to control. Furthermore, more or less decomposition takes place. On repeating the reaction the substances were mixed, in very small portions, in a large test-tube and stirred with a glass rod. After the reaction, water and ether were added and the tube was shaken. The ether was found to contain a little oil in a very impure state and in quantity insufficient for distillation. It was neutral and insoluble in water, however, and there seems to be no reason for doubting that it was the diethyl ether.

#### VI. Action of Benzene and Aluminium Chloride.

The action of benzene on the chlorides, in the presence of aluminium chloride, was first studied by Remsen and Saunders.<sup>1</sup> They showed that the high-melting chloride reacts to form, as the final product, orthobenzoyldiphenylsulphone, as follows:



This substance melts at 183°–184°. In studying the reaction with a mixture of the two chlorides, by far the largest portion of the product was the same substance. They obtained simultaneously, however, another compound, melting at 162°–163°. Analysis showed it to be of the same empirical formula as the first one, but its conduct, when fused with potassium hydroxide, led them to assign to it the formula of the lactone,

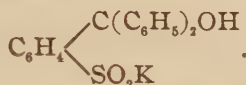


In their article upon the chlorides of orthosulphobenzoic

<sup>1</sup> Am. Chem. J. 17, 347.



acid, List and Stein<sup>1</sup> also describe the substance. They obtained it by the action of benzene and aluminium chloride upon the mixed chlorides. The reaction was allowed to proceed at the ordinary temperature for some days, after which the mixture was warmed for a time. The substance dissolved in boiling, alcoholic potassium hydroxide with the formation of a potassium salt of the formula



Upon treatment with acids the lactone was recovered.

Since it has been possible to isolate the low-melting chloride in a pure condition, many attempts have been made to prepare this substance. None of them has been successful, the sole product of the reaction being always the symmetrical compound, orthobenzoyldiphenylsulphone, identical with that derived from the high-melting chloride.

The writer made several attempts to obtain the lactone by the action of benzene and aluminium chloride upon the low-melting chloride, but always without success. The reaction was allowed to take place at the room temperature, during a period of 3 or 4 days, and also at the temperature of a boiling water-bath, when it is complete in a short time. Finally, a mixture of 60 per cent of the low-melting chloride and 40 per cent of the high-melting chloride was dissolved in pure, dry benzene, and aluminium chloride was added from time to time. The reaction was allowed to proceed at the room temperature. The resulting product was found to be symmetrical however, no trace of the lactone being formed. The proportion of the two chlorides taken is about that in which they occur in the mixture which is obtained by the action of phosphorus pentachloride on the acid potassium salt. It was with this mixture that List and Stein obtained their results.

From the experiments of former workers, as well as from those last recorded, it would seem doubtful if the product first described by Remsen and Saunders, and later by List and Stein, was in reality the lactone as supposed. A substance has been obtained by another method, however, and will be

<sup>1</sup> Ber. d. chem. Ges., 31, 1648.

described presently, which analysis shows to be the lactone and which, moreover, agrees with the description of the lactone made as above. Such being the case, the conclusion must be that the action of benzene and aluminium chloride has, in two instances at least, given the lactone. From the failure of other workers to obtain it, it is evident that peculiar conditions must be necessary to its formation.

### *VII. Experiments with Thionyl Chloride.*

Since the methods which are employed for the preparation of the chlorides, especially in the case of the low-melting one, fail to give satisfactory yields, it seemed desirable to try the action of thionyl chloride on both the acid and neutral salts, in the hope that this reagent might give better results than the pentachloride or oxychloride of phosphorus.

Ten grams of the dried and finely pulverized neutral potassium salt of orthosulphobenzoic acid were placed in a small balloon flask, and an equal weight (2.5 mol.) of thionyl chloride was added. The flask was fitted to a return condenser, which was provided at its upper end with a Peligot tube containing a strong solution of sodium hydroxide, to absorb the sulphur dioxide which was given off. The reaction started without the application of heat, but did not become vigorous. At the temperature of the boiling water-bath, however, it progressed rapidly. The heating was continued until no more sulphur dioxide was liberated, about 45 minutes being required. During the progress of the reaction the mass became more and more viscous, until at the end the appearance had become like that of thick starch paste. The condenser was then reversed and the excess of thionyl chloride was distilled off. This process was much facilitated by slightly diminishing the pressure. After the removal of the excess of thionyl chloride, the mass became crystalline. It was removed from the flask and ground in a mortar with water containing ice, and then poured into a separating funnel and shaken with ice-water and ether. A portion of the material did not immediately go into solution but dissolved gradually, as the shaking was continued. After removing the ethereal layer it was examined with the expectation of finding one or both of the chlorides of orthosulphobenzoic

acid. All that was obtained, however, was a small quantity of the anhydride of orthosulphobenzoic acid which had escaped hydrolysis in the treatment with water. A portion of the material, which did not dissolve readily, was filtered off and examined. It was found to contain potassium and chlorine, and to show an acid reaction with litmus. On boiling with water it was dissolved and hydrochloric acid was formed. A small quantity was dried on a porous plate and placed in a desiccator over sulphuric acid. It was hoped in this way to obtain a specimen for analysis in fairly pure condition, but upon opening the desiccator, some hours later, fumes of hydrochloric acid escaped, showing that the substance had been hydrolyzed. No further effort was made to obtain the pure compound, but its composition was shown by another method.

The reaction between the neutral salt and thionyl chloride was repeated in the manner above described, but after distilling off the excess of the latter, absolute alcohol was added and the mixture boiled. At the end of an hour the alcohol was filtered off. Upon cooling, crystals separated in the form of thin leaves, these were removed and analyzed for potassium :

0.1050 gram substance gave 0.334 gram  $K_2SO_4$ .

| K | Calculated for<br>$C_6H_4 \begin{cases} COOC_2H_5 \\ SO_2OK \end{cases}$ | Found. |
|---|--------------------------------------------------------------------------|--------|
|   | 14.59                                                                    | 14.28  |

The yield of these crystals was only about 0.5 gram, showing that the reaction had, for the most part, progressed beyond the first stage. That even a small quantity of this salt was obtained, however, points conclusively to the presence of a

compound of the formula  $C_6H_4 \begin{cases} COCl \\ SO_2OK \end{cases}$ . That the structure

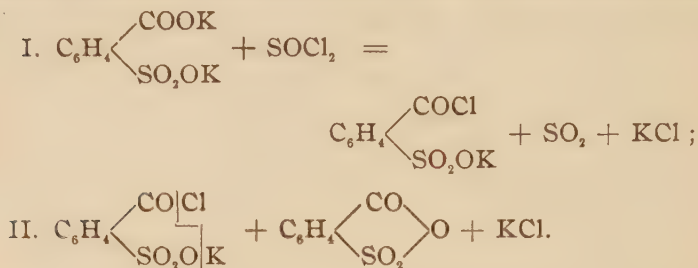
of this monochlorinated derivative of the neutral potassium salt is that which has been assigned to it, rather than that of the

isomeric sulphone chloride,  $C_6H_4 \begin{cases} COOK \\ SO_2Cl \end{cases}$ , is evident from the

fact that it is converted into an ester upon boiling with alco-

hol, a reaction which does not occur with the sulphone chlorides.

The formation of the anhydride, then, takes place in two stages, the first product being a monochlorinated derivative which passes into the anhydride by loss of potassium chloride :



The next experiment was performed with the intention of determining whether or not the anhydride could profitably be prepared by this method. Thirty-four grams of the neutral potassium salt were treated with a large excess (5 or 6 mols.) of thionyl chloride and heated on the water-bath until no more sulphur dioxide escaped. About one hour was required. The excess of thionyl chloride was then distilled off and the residue in the flask was extracted with dry benzene. Only 7 grams (31 per cent) of the anhydride were obtained, however. It is probable that if the heating had been allowed to proceed longer, the yield would have been larger, but the experiment was not repeated with the neutral salt, since the acid salt was found to give much more satisfactory results.

The final experiment with the neutral salt was an attempt to prepare a chloride of orthosulphobenzoic acid. Twenty grams of thionyl chloride were poured into a Carius tube, an equal weight of the neutral salt added and a thorough mixture made. After heating at 125°, for 13 hours, the tube was opened and found to contain anhydride, but no chloride was present. In order to isolate the chloride, if formed, the reaction mixture was shaken with water, ice and ether. Since the greater part of the anhydride was hydrolyzed by this process, the quantity formed was not determined.

*Experiments with the Acid Salt.*—Both the neutral and acid potassium salts of orthosulphobenzoic acid are attacked with



about the same ease by thionyl chloride. With the acid salt the reaction takes place with the formation of hydrochloric acid, showing that the point of attack is the carboxyl. With the acid salt, as with the neutral, no chloride was obtained either under the ordinary pressure or in a sealed tube. As a method of preparing the anhydride, however, the action of thionyl chloride was found to be very satisfactory. Two experiments were conducted; in the first, 10 grams of the acid salt were heated on the water-bath with a large excess of thionyl chloride. The reaction was complete in 45 minutes. After distilling off the excess of thionyl chloride, the residue was extracted with dry benzene. Four grams of the anhydride were obtained, which corresponds to a yield of 52 per cent.

The second experiment was conducted with somewhat larger quantities. Twenty-seven grams of the acid salt were heated on the water-bath with 56 grams of thionyl chloride. The volatile reaction products ceased to escape in about an hour, but the mixture was heated for 1.5 hours longer, and was then treated in the usual way. Sixteen and five-tenths grams (80 per cent) of the anhydride were obtained.

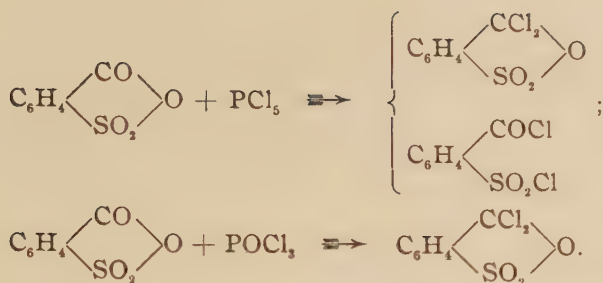
In order to get the best results, it has been found advisable to use a large excess of thionyl chloride, by so doing the mixture remains in a semi-liquid state, and better contact is secured. It is also advisable to heat for an hour or two after the volatile reaction products have ceased to escape. The thionyl chloride recovered is quite pure and may be used again.

The results of these experiments indicate that the normal reaction of chlorinating agents on both the acid and neutral salts is the formation of a monochlorinated derivative containing the chlorine in combination with the carbonyl. This passes into the anhydride by the loss of potassium chloride. The formation of the two dichlorides of orthosulphobenzoic acid remains to be explained. In the preparation of the high-melting chloride, about 60 per cent of the low-melting chloride is also produced. When the neutral salt is treated in the same manner a mixture is also obtained. In this case the chlorinating agent is phosphorus pentachloride. On the other hand, in the preparation of the low-melting chloride

by the action of phosphorus oxychloride on the neutral salt, practically none of the high-melting chloride is formed. The formation of the high-melting chloride, then, is favored by the action of a powerful chlorinating agent.

List and Stein<sup>3</sup> have shown that the action of phosphorus pentachloride on the anhydride at high temperatures, gives rise to the formation of both chlorides. For the sake of comparison the action of the oxychloride upon the anhydride was tried. Twelve grams of the anhydride were heated for 14 hours with phosphorus oxychloride at 125°. At the end of that time the mixture was examined and it was found that, while the reaction was by no means complete, about 2 grams of the low-melting chloride had been formed. It was identified by its melting point. In order to test for the presence of high-melting chloride, ammonia was added but no sweet taste was produced. The action of phosphorus pentachloride probably takes place as follows. The anhydride is first formed and it is attacked in two ways by the pentachloride, with the formation of two isomeric substances. The action of the oxychloride can take place in only one way, however, since only one product is formed. If the action of the oxychloride were not considered, one might assume that with the pentachloride the reaction all goes in one direction, and that a rearrangement takes place. The fact that neither chloride can be changed into the other by heat, also argues against the latter supposition. The pentachloride, then, must have the power to chlorinate both the carbonyl group of the anhydride and also to replace the anhydride oxygen atom. It would be expected that the latter reaction would take place with the greater difficulty and, as already stated, the yield of high-melting chloride, when prepared from the acid salt, is only 40 per cent of the total. The oxychloride can only attack the carbonyl group, while, as has been shown, thionyl chloride does not react with the anhydride:

<sup>3</sup> *Proc. & Chem. Soc.*, 21, 1032.



### VIII. Experiments with Magnesiumphenyl Bromide.

*Action on the High-Melting Chloride.*—With the high-melting chloride magnesiumphenyl bromide reacts only at the boiling point of ether, while with the low-melting chloride the reaction is so violent that the solutions must be cooled with ice and mixed very slowly. The resulting products are very difficult to purify. In the case of the high-melting chloride the product has been fully identified, while with the low-melting chloride satisfactory results have not been obtained.

Ten grams of the high-melting chloride were dissolved in dry ether, and to the solution an ethereal solution of 3.5 molecules of magnesiumphenyl bromide was added. The mixture was boiled for an hour or two until the oily substance which settled to the bottom of the flask did not increase in quantity. At this point the ether above the oil had become clear. The ether was then poured off and the residue in the flask was shaken with water and dilute hydrochloric acid. After the decomposition had been effected, the resulting oil was allowed to settle and the water and acid were poured off. It was washed with several changes of water. Steam was then conducted into the flask to remove any brombenzene which might have been present. After many unsuccessful attempts to purify this oil, the following method was found satisfactory: The oil was allowed to stand under water for a week or more. At the end of this time it had usually solidified, for the most part. It was then heated to boiling with methyl alcohol and the alcohol poured off while still hot. This treatment removed the un-solidified portion. The solid remaining was then crystallized from ethyl alcohol. The oil is easily soluble in alcohol and

ether. After solidification, however, it is soluble in these liquids with much greater difficulty.

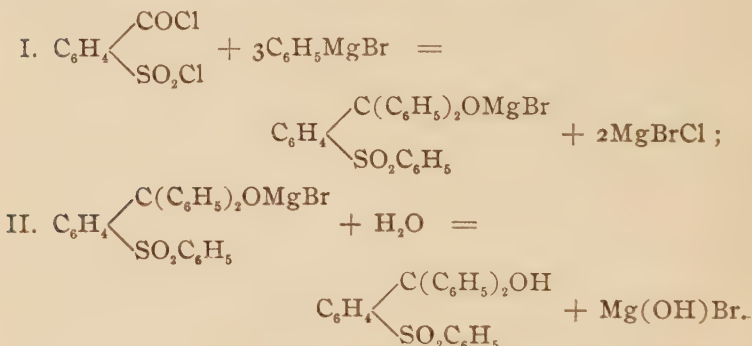
The product which had been crystallized from alcohol melted at  $183^{\circ}$ – $184^{\circ}$ . It is not affected by alcoholic potassium hydroxide. With concentrated nitric and sulphuric acids a dark red color is produced, an indication of the carbinol condition. Analysis :

0.1284 gram substance gave 0.3509 gram  $\text{CO}_2$  and 0.0603 gram  $\text{H}_2\text{O}$ .

0.2146 gram substance gave 0.1268 gram  $\text{BaSO}_4$  (Carius).

|   | Calculated for<br>$\text{C}_6\text{H}_4\begin{cases} \text{C}(\text{C}_6\text{H}_5)_2\text{OH} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{cases}$ | Found. |
|---|------------------------------------------------------------------------------------------------------------------------------------------------|--------|
| C | 74.95                                                                                                                                          | 74.52  |
| H | 5.04                                                                                                                                           | 5.26   |
| S | 8.00                                                                                                                                           | 8.11   |

The reaction must be represented as follows :



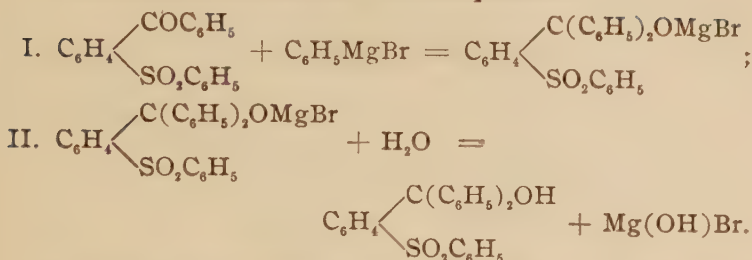
The structure of this substance was established by treating orthobenzoyldiphenylsulphone with magnesiumphenyl bromide. The product thus obtained melted at the same temperature, and the melting point of a mixture of the two preparations remained unchanged. Analysis :

0.1378 gram substance gave 0.3783 gram  $\text{CO}_2$  and 0.0661 gram  $\text{H}_2\text{O}$ .

|   | Calculated for<br>$\text{C}_6\text{H}_4\begin{cases} \text{C}(\text{C}_6\text{H}_5)_2\text{OH} \\ \text{SO}_2\text{C}_6\text{H}_5 \end{cases}$ | Found. |
|---|------------------------------------------------------------------------------------------------------------------------------------------------|--------|
| C | 74.95                                                                                                                                          | 74.86  |
| H | 5.04                                                                                                                                           | 5.37   |



The reaction is represented by the equations :



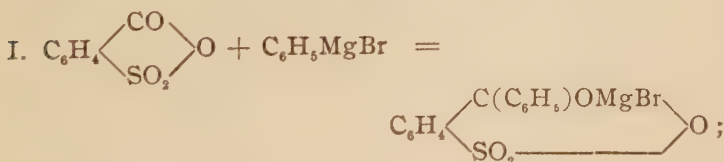
*Action on Sulphobenzoic Anhydride.*—The reaction of magnesiumphenyl bromide on sulphobenzoic anhydride was tried, in the hope of obtaining a diphenylated derivative. This product was obtained and has been referred to under the reaction of benzene and aluminium chloride. The action is vigorous, and the solutions should be cooled with ice. After standing some time, water and sulphuric acid were added and the contents of the flask were well shaken with ether. Upon examination of the ethereal layer a product was obtained which, when crystallized from alcohol, melted sharply at  $163^\circ$  (uncorr.). It dissolved in alcoholic potassium hydroxide, on boiling, with the formation of a salt soluble in water. Upon acidification the original substance was precipitated. Neither water nor aqueous potassium hydroxide would dissolve the substance even when boiled. Analysis :

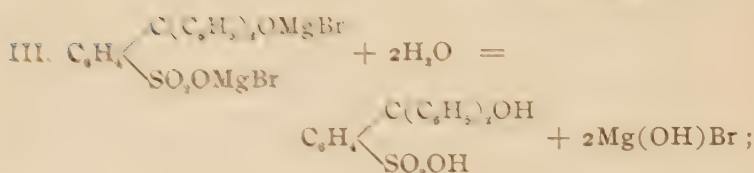
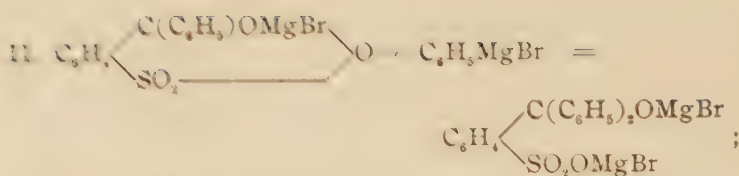
0.1070 gram substance gave 0.2772 gram  $\text{CO}_2$  and 0.0447 gram  $\text{H}_2\text{O}$ .

0.2056 gram substance gave 0.1564 gram  $\text{BaSO}_4$  (Carius).

|   | Calculated for<br>$\text{C}_6\text{H}_4 \begin{array}{l} \text{C}(\text{C}_6\text{H}_5)_2 \\ \text{SO}_2 \end{array} \text{O}$ . | Found. |
|---|----------------------------------------------------------------------------------------------------------------------------------|--------|
| C | 70.76                                                                                                                            | 70.64  |
| H | 4.38                                                                                                                             | 4.68   |
| S | 9.95                                                                                                                             | 10.40  |

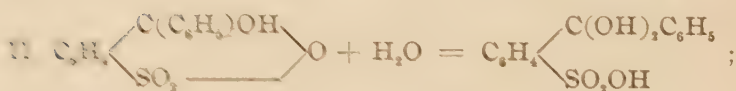
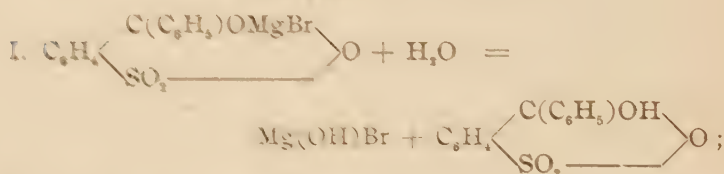
The reaction may be expressed as follows :





The substance just described is formed to the extent of only about 10 per cent. It is probable that the reaction, in the main, stops at stage I. The product would then be hydrolyzed

to form the acid,  $\text{C}_6\text{H}_5 \begin{array}{l} \diagup \text{COC}_6\text{H}_5 \\ \diagdown \text{SO}_2\text{OH} \end{array}$ , as follows :

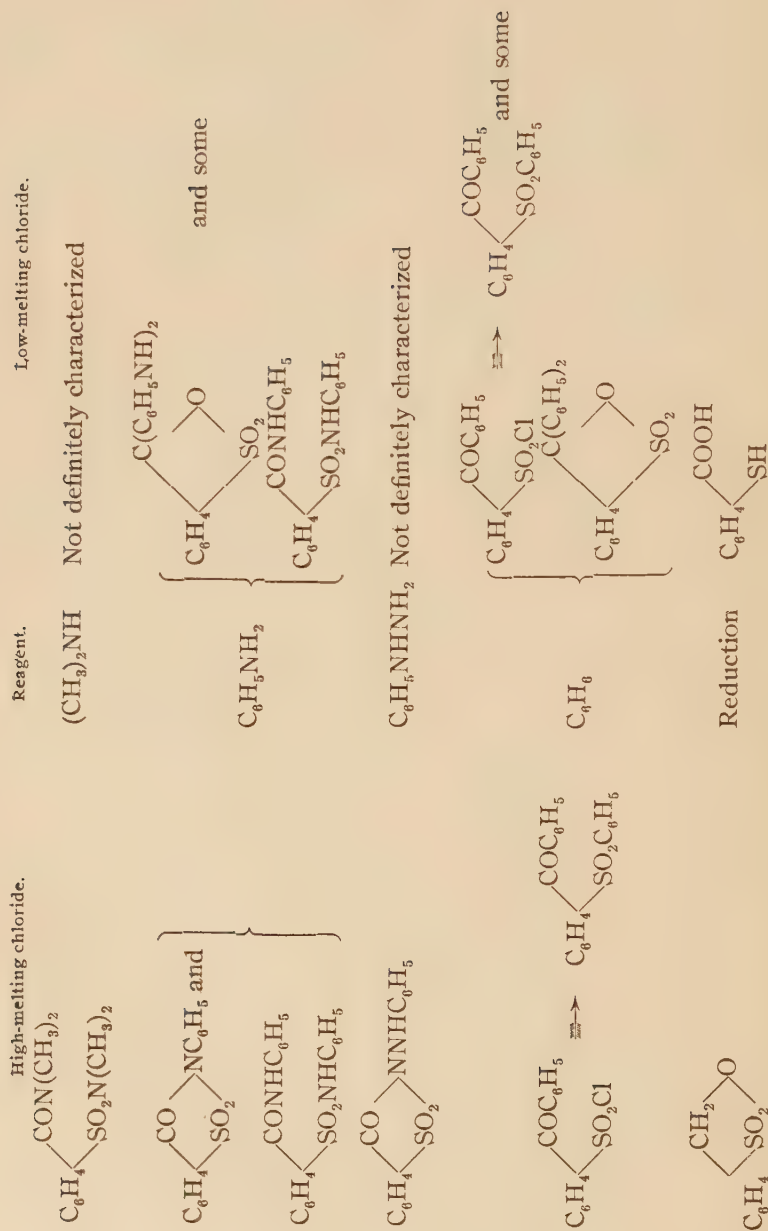


This compound is not of any special interest and no attempt was made to separate it. Since the substance is soluble in water, it did not appear in the ethereal extract of the products.

#### IX. Summary of Previous Investigations.

The more important reactions of the chlorides are as follows :







### X. Conclusions.

From this table it will be seen that with water, the alcohols and alcoholates both chlorides give the same products and that they are symmetrical. Benzene and aluminium chloride have undoubtedly yielded an unsymmetrical derivative in at least two instances, but the tendency is to form the same symmetrical product with both chlorides.

In contrast to these reactions are those of ammonia and the amines. With the high-melting chloride, the products always indicate its symmetrical nature. With the low-melting chloride, however, the products may vary with the conditions, or both the symmetrical and unsymmetrical products may be found in the same reaction. These facts indicate that the products pass from the unsymmetrical to the symmetrical, and not in the opposite direction.<sup>1</sup> The conclusion must be, then, that the stable form of the derivatives is the symmetrical. The unsymmetrical form may be unstable to such a degree that it cannot exist as in the case of the esters, and alcoholic derivatives in general. With the nitrogen derivatives there is a greater degree of stability, and the unsymmetrical forms are found to exist. The tendency to pass into the stable form, however, is shown here by the fact that both isomers are found in the same reaction.

It should be borne in mind that no conclusion can be drawn concerning the structure of the chlorides from any one reaction. From the results of the many investigations here tabulated the only rational conclusion seems to be that the chlorides are distinct chemical individuals, the one melting at 79°.5 being symmetrical, the one melting at 40° being unsymmetrical.

*The Chlorides of Dibasic Acids in General.*—In order to show the analogies which exist between the chlorides of orthosulphobenzoic acid and those of certain other dibasic acids, a brief account of the conduct of the latter has been prepared.

The chlorides of dibasic acids of the aliphatic series which have been most extensively studied are those of succinic, malonic and glutaric acids, while in the aromatic series, phthalyl

<sup>1</sup> One exception to this general rule is known. When either chloride is heated with resorcinol, sulphone fluorescein, an unsymmetrical substance is produced.

chloride and the chlorides of orthosulphobenzoic acid have been most carefully investigated.

Phthalyl chloride was first prepared by Müller,<sup>1</sup> by allowing phosphorus pentachloride to act upon phthalic acid, or its anhydride. He treated the chloride thus obtained with water, and regenerated the original acid. Kolbe and Wischin<sup>2</sup> reduced the chloride by means of zinc and aqueous hydrochloric acid, and obtained, as they supposed, an aldehyde of the

formula  $\text{C}_6\text{H}_4 \begin{matrix} \diagup \text{CHO} \\ \diagdown \text{CHO} \end{matrix}$ . This was shown later by Hessert<sup>3</sup> to

correspond rather to the reactions of a lactone than of an aldehyde, and accordingly he assigned to it the formula of

phthalide,  $\text{C}_6\text{H}_4 \begin{matrix} \diagup \text{CH}_2 \\ \diagdown \text{CO} \end{matrix} \text{O}$ . A short time after this Friedel

and Crafts<sup>4</sup> allowed benzene to react upon phthalyl chloride in the presence of aluminium chloride, and obtained a diphenylated derivative which they supposed was to be represented by the formula  $\text{C}_6\text{H}_4 \begin{matrix} \diagup \text{COC}_6\text{H}_5 \\ \diagdown \text{COC}_6\text{H}_5 \end{matrix}$ . Baeyer,<sup>5</sup> who was

engaged at this time upon the study of the phthaleins, having had occasion to prepare this substance, found that when boiled with alcoholic potash it dissolved with the formation of the potassium salt of an oxyacid. Upon treatment with acids the original substance was precipitated. While these changes pointed clearly to the lactone formula for the compound, Baeyer sought still further evidence. He accordingly reduced the above potassium salt by means of zinc in alkaline solution, and obtained a carboxyl acid, which when distilled with barium hydroxide gave him triphenylmethane. The reactions involved must be expressed as follows:

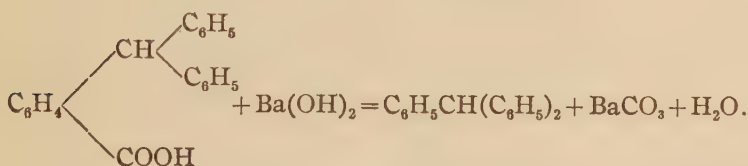
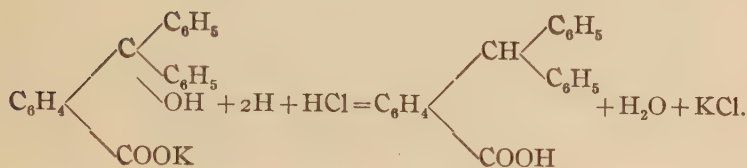
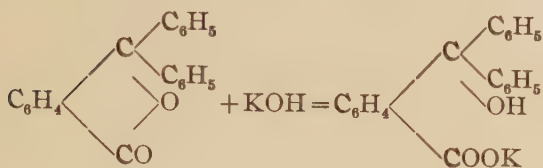
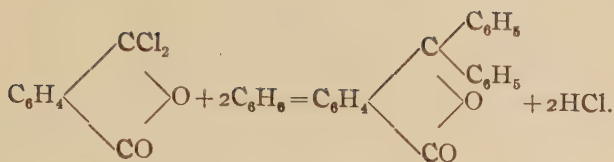
<sup>1</sup> Zeit. Chem. Pharm. 1863, p. 257.

<sup>2</sup> Z. Chem. (2) II, 315.

<sup>3</sup> Ber. d. chem. Ges. 10, 1445.

<sup>4</sup> Compt. rend. June 11, 1877.

<sup>5</sup> Ann. Chem. 202, 50.



Friedel<sup>1</sup> taking into consideration the formation of phthalide proposed to ascribe the unsymmetrical formula to phthalyl chloride, thus removing the difficulty in the interpretation of the above reaction.

Since the reactions in the presence of aluminium chloride, are often attended by molecular rearrangements it was thought possible that the formation of the unsymmetrical diphenyl derivative might be due to this cause. This objection was removed, however, by Nölting and Bechi<sup>2</sup> who obtained the same product by the action of mercury diphenyl.

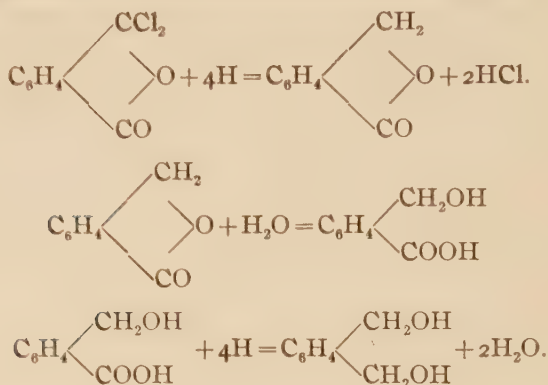
These facts point unmistakably to the unsymmetrical formula for phthalyl chloride. There are, on the other hand, certain facts which seem to point toward the symmetrical formula for this substance.

<sup>1</sup> Bull. Soc. Chim. **32**, 595.

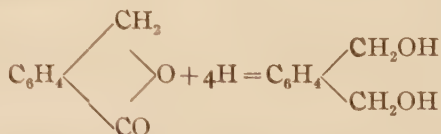
<sup>2</sup> Ber. d. chem. Ges. **17**, 385.

In his article upon the chlorides of dibasic acids Auger<sup>1</sup> discusses these objections and gives an account of his own experiments on this and other analogous substances.

(1) The formation of the orthophthalyl alcohol by reduction with sodium amalgam in acetic acid, a reaction seeming to point to the symmetrical formula, he thinks may indeed be the normal reaction of an unsymmetrical structure, thus:



or more simply:



(2) The question of the identity of the esters of phthalic acid whether prepared from the silver salt and an alkyl iodide, or by means of the chloride and an alcoholate, has been settled by Graebe,<sup>2</sup> who found them to be identical whether prepared by one method or the other. In the case of the esters of tetrachlorophthalic acid, however, Graebe found isomerism.

The action of ammonia upon phthalyl chloride has been the subject of several investigations. Kuhara<sup>3</sup> mixed the chloride with ammonia, and after the reaction had taken place added hydrochloric acid in excess. He then heated the mixture in

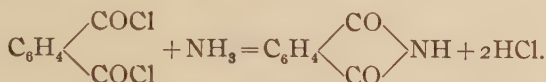
<sup>1</sup> Ann. Chim. Phys. (6) **22**, 289.

<sup>2</sup> Ber. d. chem. Ges. **16**, 860.

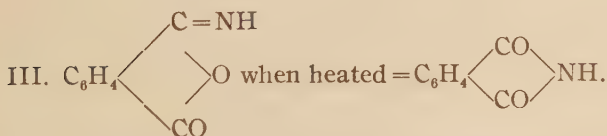
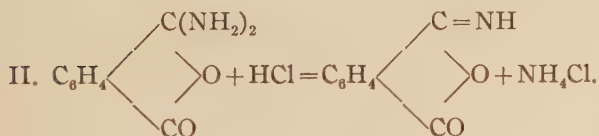
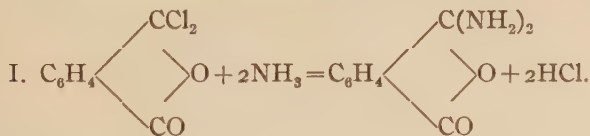
<sup>3</sup> Am. Chem. J. **3**, 26.



order to dissolve the precipitate which had been formed upon the addition of the acid. Upon cooling, ordinary phthalimide crystallized out. He also obtained on one occasion a substance isomeric with phthalimide melting at  $192^{\circ}$ . These experiments could best be interpreted by assuming the symmetrical formula for phthalyl chloride:



In repeating the work of Kuhara, Auger<sup>1</sup> obtained quite different results. He isolated a substance which he considered to be the unsymmetrical diamide and from it by the action of hydrochloric acid he passed to what he supposed to be the corresponding imide. This imide melted at  $145^{\circ}$  to a clear liquid which soon solidified and subsequently melted at  $228^{\circ}$ , the melting-point of the symmetrical imide. He represented the reactions as follows:

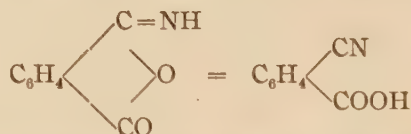


Had these reactions remained unquestioned they would have been regarded as strong evidence for the unsymmetrical formula of the chloride. In a later investigation Hoogewerff and Van Dorp<sup>2</sup> showed that Auger was dealing with an impure substance, and that the product formed by the action of

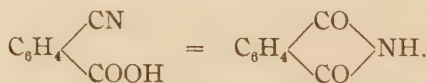
<sup>1</sup> Loc. cit.

<sup>2</sup> Rec. Trav. Chim. II, 84.

ammonia on the chloride is in reality orthocyanbenzoic acid. It was this substance in the impure state which Auger had described as the unsymmetrical imide. The pure cyan acid melts between  $180^{\circ}$  and  $190^{\circ}$ , depending upon the rapidity of the heating, and is transformed into the symmetrical imide. This transformation is also effected by boiling with water. Kuhara had obtained the cyan acid once in a pure condition, but his failure to obtain it a second time lay in the method of purification which he adopted. As has been said, boiling with water converts the acid into the symmetrical imide, and it was this substance which Kuhara obtained from the reaction. Hoogewerff and Van Dorp believe that the conversion of the chloride into the cyan acid takes place as follows. The first action of the ammonia causes the formation of an unsymmetrical imide, which is unstable in the alkaline solution and immediately passes into the cyan acid by a molecular rearrangement:



The transformation of the cyan acid into the symmetrical imide is also accompanied by a molecular rearrangement:

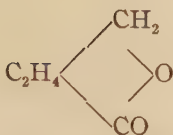


The weight of evidence seems to argue so strongly for the unsymmetrical nature of phthalyl chloride that little if any doubt of its correctness can exist.

*Succinyl Chloride.*—Succinyl chloride was discovered by Gerhardt and Chiozza.<sup>1</sup> The reduction of the chloride was first studied by Saytzeff, who regarded the product thus obtained as succinic aldehyde, in consideration of certain of its reactions; and it was not until 1880 that Brecht<sup>2</sup> pointed out that its chemical conduct placed it in the class of lactones. He accordingly assigned to it the formula:

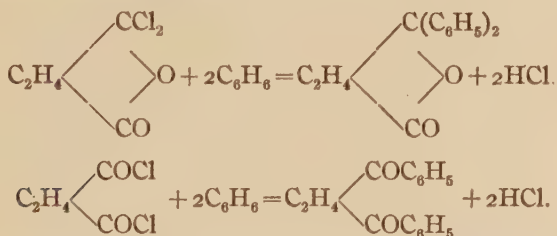
<sup>1</sup> Ann. Chem. 87, 293.

<sup>2</sup> Ber. d. chem. Ges. 13, 748.



analogous to phthalide. In the same year this conclusion was reached by Saytzeff by a different method.

In studying the action of benzene, in the presence of aluminium chloride, upon succinyl chloride, Auger observed that while 90 per cent. of the reaction product was, as in the case of phthalyl chloride, a lactone, a small quantity, about 10 per cent., of the isomeric symmetrical product was always obtained. The former must then be derived from a chloride of the unsymmetrical variety, while the latter is derived from the symmetrical chloride thus:



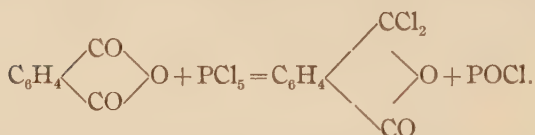
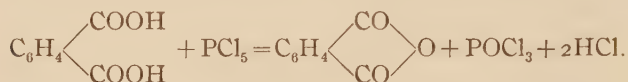
In the reactions with ammonia Auger describes the formation of an unsymmetrical diamide and imide as in the case of phthalyl chloride. It is probable that his observations were in error,<sup>1</sup> however, and that the reaction proceeds as has been pointed out in the latter case by Hoogewerff and Van Dorp.

The chloride of malonic acid was prepared by Auger by allowing thionyl chloride to react upon the free acid. The chloride was submitted to investigation with the purpose of determining whether it too was of the unsymmetrical structure. The reaction of benzene and aluminium chloride gave as the final product dibenzoyl methane, a symmetrical compound. Among the reactions already known, the condensation of malonic acid and urea in the presence of the oxychloride of phosphorus to form barbituric acid, pointed to the symmetrical formula for the chloride of malonic acid. With the chloride

<sup>1</sup> Vorländer: Ber. d. chem. Ges. 30, 2268 (note).

of ethyl malonic acid the reactions with all reagents were found to be analogous.

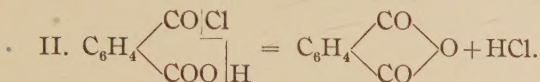
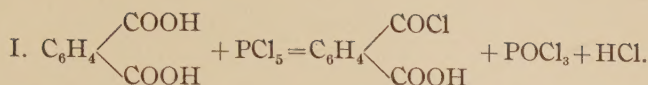
In the cases just considered, it is seen that those acids from which unsymmetrical chlorides have been obtained are those having their carboxyl groups in the  $\gamma$  or 1-4 positions. Since these acids form anhydrides, the formation of unsymmetrical chlorides may be explained by assuming the intermediate formation of the anhydride and the subsequent action upon it by the chlorinating agent used:



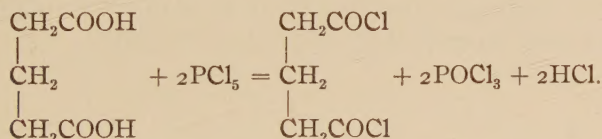
On the other hand there is a possibility that the intermediate formation of an anhydride does not govern the formation of the unsymmetrical chloride, but that the  $\gamma$ -position of the carboxyls is the determining influence. In order to test this point Auger resorted to glutaric acid. Here the carboxyl groups are in the 1-5 or  $\delta$ -position. The acid forms an anhydride on simple distillation, however. The pentachloride of phosphorus would in all probability bring about this change, and the resulting chloride would be unsymmetrical if its formation is conditioned by the presence of anhydride. An examination of the chloride of glutaric acid showed it to be symmetrical, however, no trace of an isomeric substance being found. Auger therefore concludes that the formation of unsymmetrical chlorides from the 1-4 carboxylic acids is due to the influence of this position of the carboxyls and is not dependent upon the intermediate formation of the anhydride.

Another explanation of the facts above referred to seems possible to the present writer. The formation of anhydride by the action of phosphorus pentachloride on organic acids probably takes place in two steps as follows:





The chlorination of only one of the carboxyl groups is due to the fact that they are in the ortho position. With succinic acid the same tendency would be present. The tendency to form anhydrides becomes less as the distance between the carboxyl groups is increased, glutaric acid being the last member of a series to yield an anhydride on simple distillation. In the aromatic series meta and para anhydrides are not formed. With the decreasing tendency to form anhydrides the tendency to form unsymmetrical chlorides disappears, a fact which can be explained by assuming that the removal of the interfering proximity of the carboxyls leaves both of them susceptible to the simultaneous attack of the chlorinating agent. This would result in the formation of a symmetrical chloride as follows:



The formation of unsymmetrical chlorides from 1-4 acids may then be dependent upon the intermediate formation of the anhydride.

### BIOGRAPHICAL.

Philip Howard Cobb was born in Portland, Maine, November 15, 1880. His early education was received in the public schools of that city. In the fall of 1898 he entered Bowdoin College, and was graduated in June 1902 with the degree of Bachelor of Arts. Since that time he has been engaged in the study of Chemistry at the Johns Hopkins University. His subordinate subjects have been Physical Chemistry and Mineralogy. In 1903-04 he was Assistant to Dr. Gilpin, and is at present Lecture Assistant to Prof. Renouf.





